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**GB A 2139648 GB A 2106545 GB A 2049739
GB 1257015**

(58) Field of search
**C7F
Selected US specifications from IPC sub-class
C23C**

(54) **Cathodic arc plasma deposition of hard coatings**

(57) Metal is evaporated using a pulsed cathodic arc source in a vacuum chamber optionally filled with a low pressure gas ambient or dopant gas to form the hard coating on the surface of the substrate. This deposition process improves the reproducibility of color and wear resistance down to very low substrate temperature (greater than or equal to about 50°C.). The films may be deposited on cosmetic or functional substrates and may consist of nitrides, carbides, and carbonitrides, of at least one of titanium, zirconium, titanium-zirconium, titanium-aluminium based on systems and doped systems of the foregoing systems. Adhesion of the coatings may be further enhanced by appropriate biasing of the substrate. The film compositions, hence color, can be suitably adjusted to eliminate the use of gold for decorative applications.

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FIG. 1

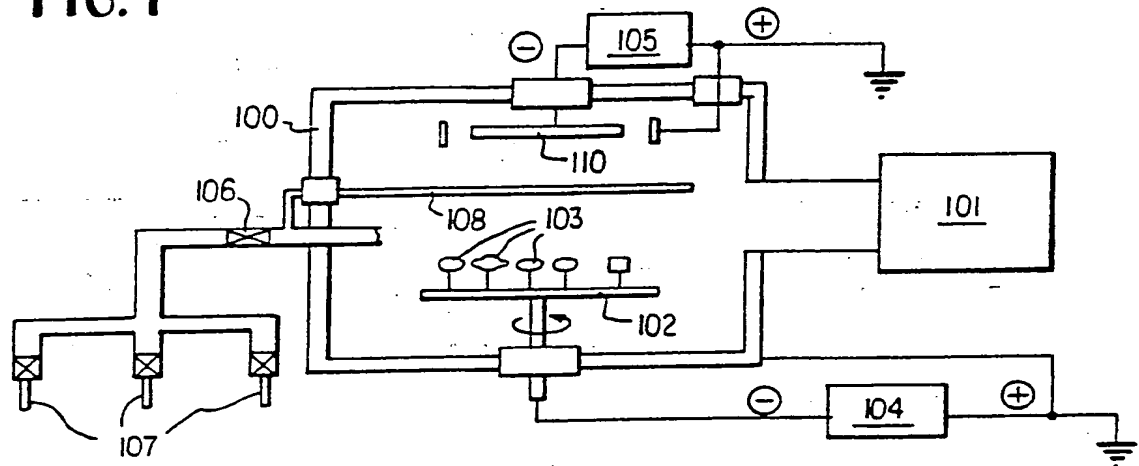


FIG. 2

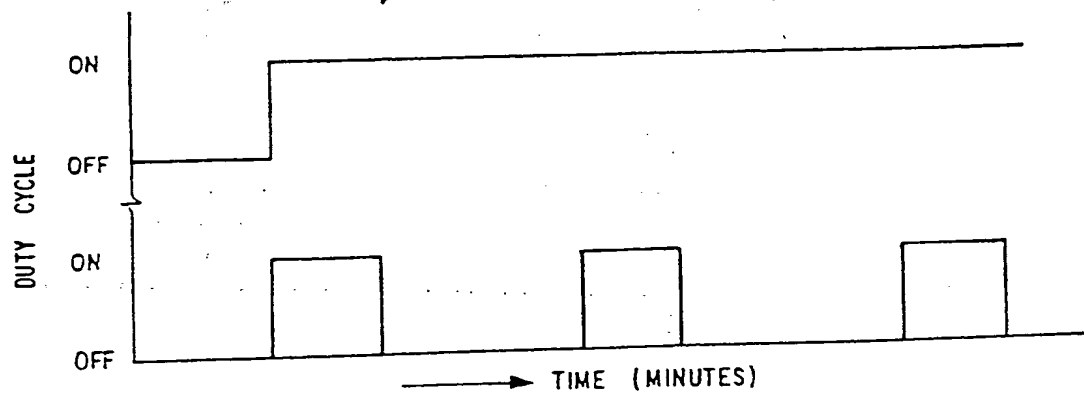
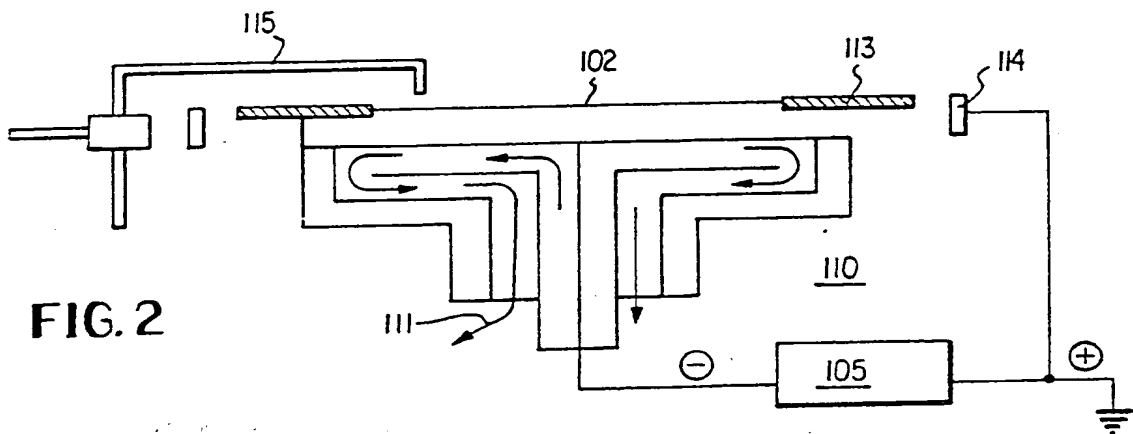


FIG. 3

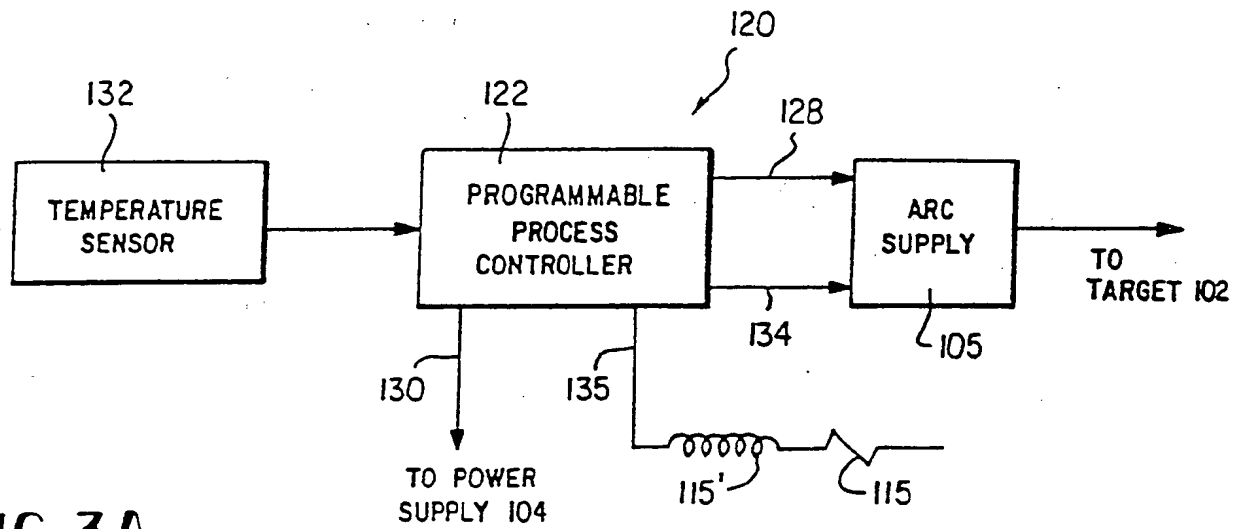


FIG. 3A

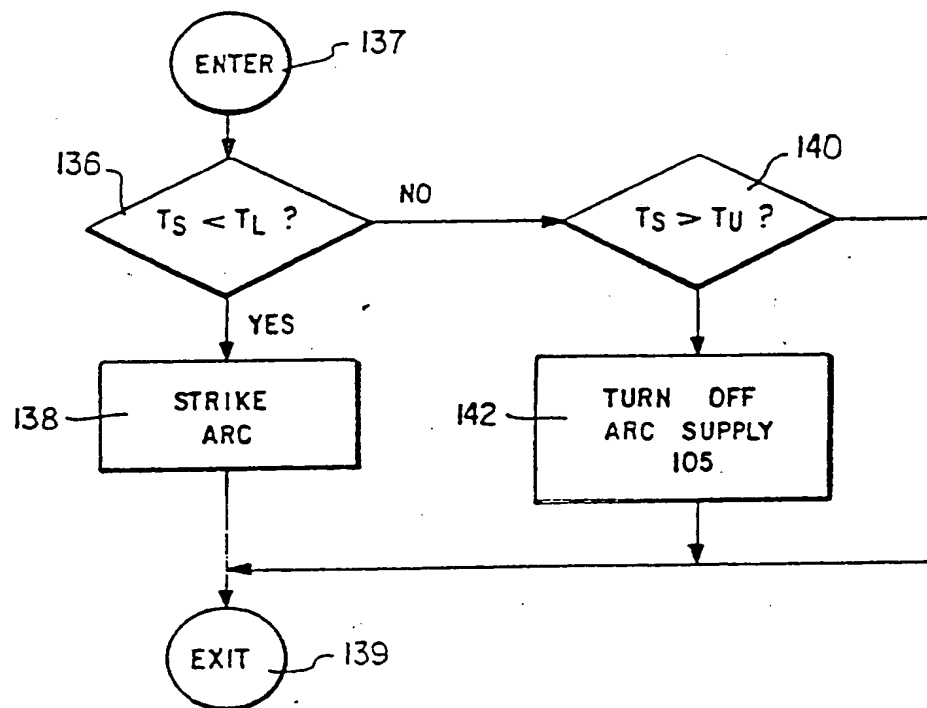


FIG 3B

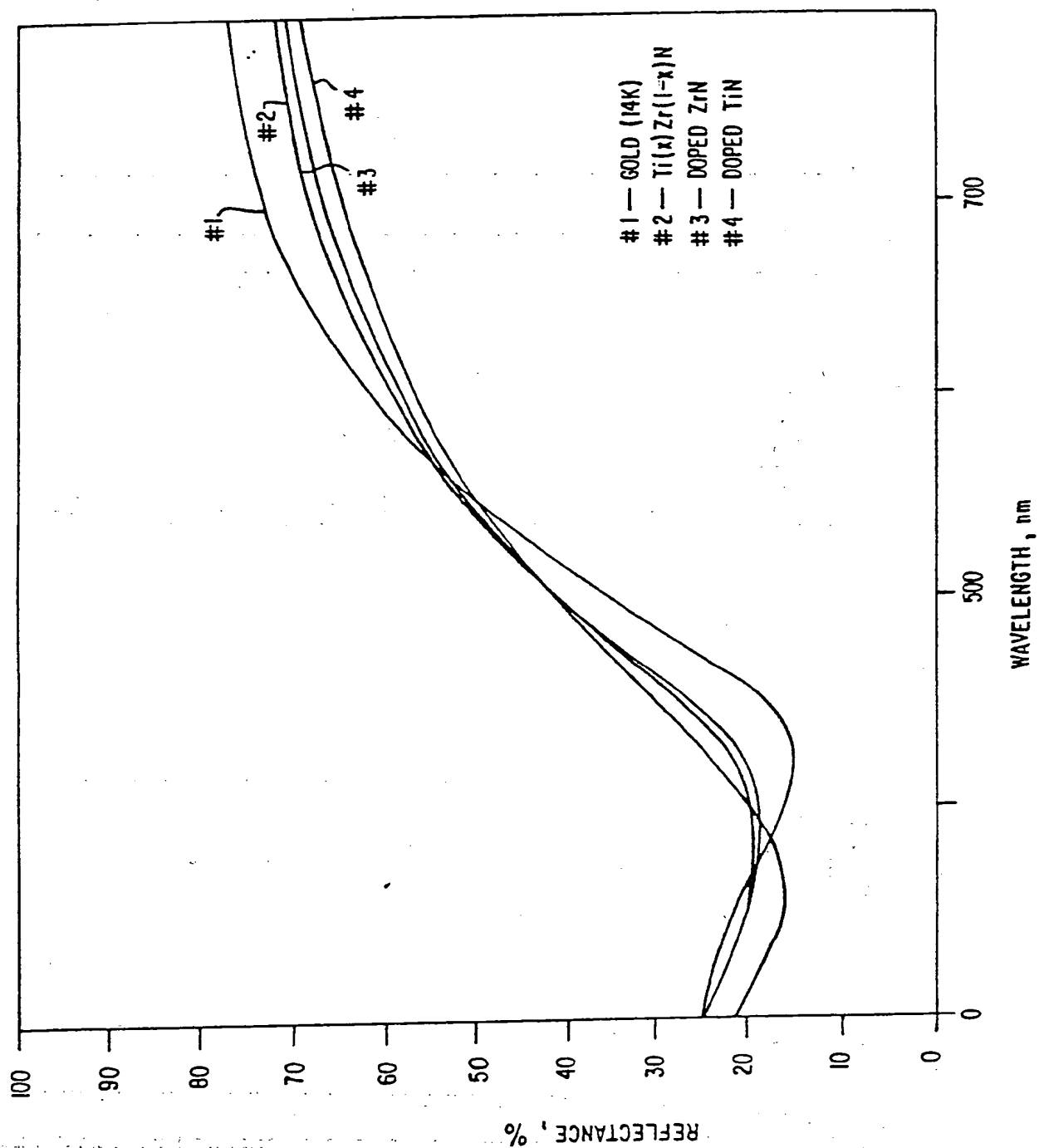


FIG. 4

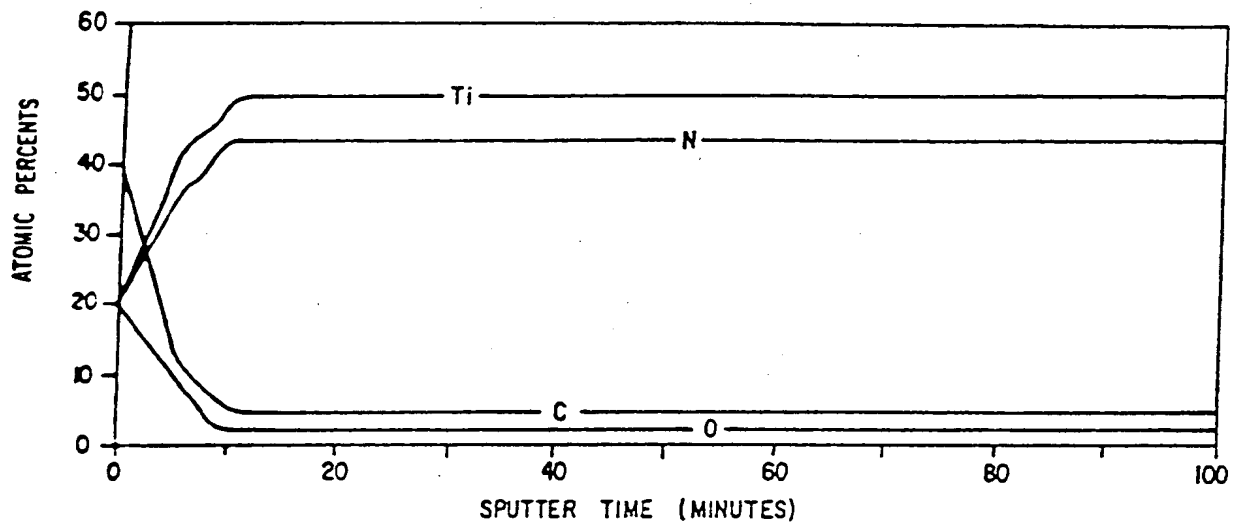


FIG.5

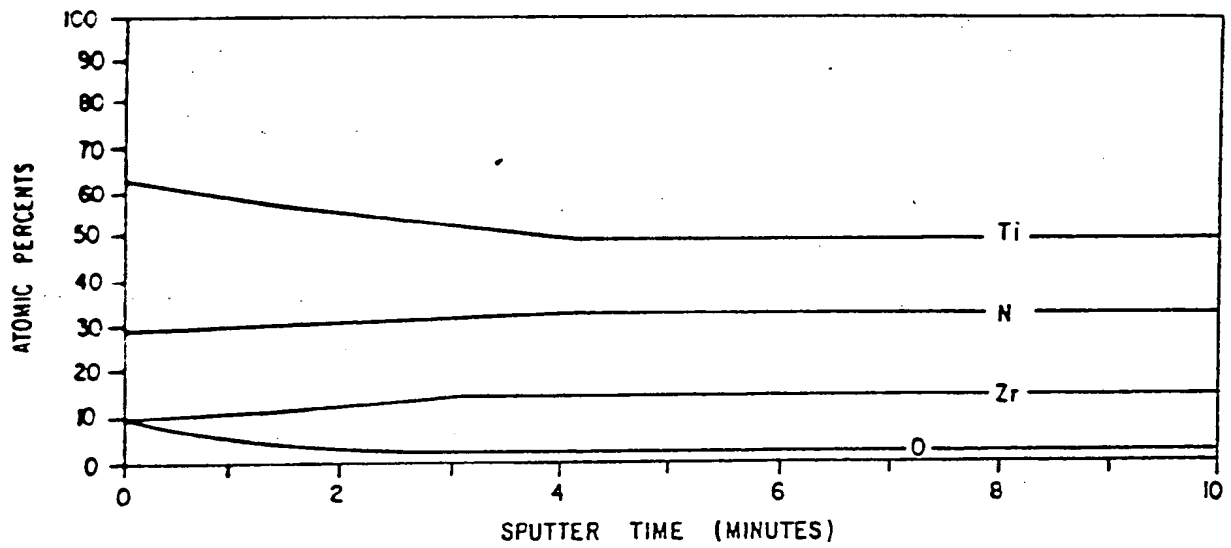


FIG.5A

"METHOD AND APPARATUS FOR VACUUM ARC PLASMA DEPOSITION OF
DECORATIVE AND WEAR RESISTANCE COATINGS"

Background of the Invention

This invention relates to a process and apparatus for coating cosmetic and functional parts to provide coatings having colors similar to gold (10k-24k) and/or a range of colors from grey, brown, bronze, black and white gold colors where the coatings have excellent adhesion and resistance or decorative coatings are class rings, watch cases and bands, lighter cases, silverware parts, automobile parts, spectacle frames, pen caps, tools and other wear (functional) parts.

Thin film materials are applied to base materials for decorative applications by either of the two methods; namely by sputtering deposition and ion plating deposition techniques. However, the typical substrate temperatures involved in both these techniques are described in U.S. Patent 4,402,994, U.S. Patent 3,900,592 and, "Journal of Vacuum Science and Technology", A, Vol. 4, No. 6, Nov/Dec., 1986, pp. 2717-2725, for example. However, many substrate materials such as plated zinc castings, brass, bearing steels, bronze and alloys containing zinc, plastics, aluminium and its alloys, etc. cannot be subjected to these high temperatures. Moreover, due to pale yellow or other pale colors generally obtained by these techniques, an overcoat of thin gold film on the surface of hard films is necessary. This is described in U.S. Patent 4,415,421. The adhesion of the interface between hard film and gold film and color reproducibility are of importance for manufacturing technologies. However,

the above processes are not always satisfactory in these regards.

Snaper U.S. Patent 3,625,848 and Sablev et al. U.S. Patent 3,793,179 disclose apparatus for metal evaporation coating with the use of a vacuum arc. Improvements thereon are described in Mularie U.S. Patent 4,430,184. The above three patents are incorporated herein by reference. Such an arc source produces coating flux that contains a high degree of ionization and has high ion energies. This results in coatings with dense microstructures and excellent adhesion. However, the conventional arc source requires a typical substrate temperature in the range of 300 - 500°C.

SUMMARY OF THE INVENTION

A primary object of the present invention is thus to provide an arc source and method for depositing decorative and wear resistance coatings down to very low substrate temperatures; which are essential for many parts, this technique not having been commercially applied to such coatings heretofore.

Another object of the present invention is to provide a method and apparatus for applying material by vacuum cathodic arc deposition onto a substrate down to very low temperatures (temperature range of about 50 - 500°C.)

Another object of the invention is to provide a method for coating a substrate with good adhesion and good decorative properties without the use of gold films.

A further object of the invention also is to provide a method for non-gold color decorative coatings using the above apparatus.

It is a further object of the invention to enhance reproducibility in color and wear resistance of decorative films on a manufacturing scale.

The method of the invention consists of placing substrates in an evacuated vessel and evaporating titanium, zirconium, titanium-zirconium, or titanium-aluminum, by action of an electric arc in the evacuated environment to produce a flux of ions, vapors and/or neutrals on the substrates. The composition of the deposits may be varied by reacting them with a suitable gas during deposition to produce a variety of films. The substrate temperature may be controlled by automatic pulsing of the arc source. The "on" time and the "off" time of the arc source may be varied to control the substrate temperature down to temperatures as low as approximately 50°C. Further, adhesion of the coatings may be improved by adjusting bias voltage on the substrate to attract ions. The coating consists of nitrides, carbides, carbonitrides of titanium, titanium-aluminum, zirconium and titanium-zirconium based systems. The color can be varied by doping the films with suitable dopants such as oxygen and carbon where the dopant gas is typically present in the range of 2 - 7 atomic percent or by using suitable reactive gas ambients. The different range of gold colors (10k - 24k) have been duplicated in Ti_xN_{1-x} or

($Ti_xZr_{1-x}N$ where $0 < x < 1$ and doped TiN or ZrN films, for example.

Other objects and advantages of this invention will be apparent from a reading of the following specification and claims taken with the drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic view of an illustrative cathodic arc plasma deposition apparatus used in the present invention.

Figure 2 is a schematic view of an illustrative arc source used in the cathodic arc plasma deposition apparatus of this invention.

Figure 3 is a time chart showing an illustrative duty cycle of the arc source of this invention.

Figure 3A is a block diagram of illustrative control circuitry for use with the arc supply of the present invention.

Figure 3B is an illustrative flow diagram of a program which may be employed with the control circuitry of Figure 3A.

Figure 4 illustrates reflectance profiles of films produced by the manufacturing process of this invention.

Figures 5 and 5A are profiles showing the atomic composition of coating films produced by the manufacturing process of this invention.

DETAILED DESCRIPTION OF PREFERRED
EMBODIMENTS OF THE INVENTION

Reference should be made to the drawing where like reference numerals refer to like parts.

The present invention overcomes the disadvantages of the prior art by improving the adhesion and color reproducibility in a cathodic arc deposition process and apparatus. Referring now in greater detail to the method and apparatus of the invention, it is applicable to the coating of a variety of substrates, including zinc, aluminum, stainless steel, plastics, brass and alloys thereof. In the hard material coated substrates according to the present invention, the surface of the tool or part is coated with at least one hard coating material selected from nitrides, carbides, carbonitrides and doped compounds thereof of titanium, zirconium, titanium-aluminum and titanium-zirconium systems.

Referring to Figure 1, an arc plasma deposition apparatus 100 of an illustrative embodiment of the invention is shown. Inside the vacuum vessel an arc source 110 is operated by an external pulsed power supply 105. The substrates 103 to be coated may be mounted on a rotary table 102. The rotary table 102 may be biased negative with an external high voltage power supply 104. Supplies 104 and 105 may be grounded or connected to appropriate sources of positive potential as indicated in Figure 1. The apparatus 100 is also equipped with a gas inlet pipe 106 and an evacuation pump system 101. A variety of gasses

may be transferred with a set of valves 107 to gas inlet pipe 106. A shutter 108 may also be employed. Further, the arc source may be partially baffled (not shown) to reduce the coating flux to control substrate temperature.

Figure 2 is a schematic diagram of an illustrative arc source 110 in which the material to be evaporated is heated with the action of an electric arc. The arc source may be arranged in the vacuum chamber in side, top, or bottom configurations. Arc confinement on the source is achieved with a confinement ring 113. The confinement ring 113 may be composed of boron nitride, titanium nitride, pyrex glass, quartz or soda lime glass. Arc confinement may also be achieved with suitable boundary shields and magnetic fields. In the latter techniques, arc extinguishment occurs and the arc is reignited automatically with a suitable electronic control, as disclosed, for example, in Sablev, et al. U.S. Patent 3,793,179. The power supply 105 may be DC if the target is conductive and RF if it is insulative.

The anode 114 is spaced from the cathode or target 102. The anode may be the outer housing of the arc source, or chamber walls or an envelope within the chamber, electrically biased or grounded. The anode 114 may be physically mounted within the chamber 100 separate from chamber walls and base and separately biased to act as the anode of the electric system as illustrated in Figure 2 and as described in U.S. Patent 3,625,848 to Snaper. Moreover, the entire chamber or an envelope thereof may

(have ground potential (see, for example, Sablev et al., U.S. Patent 3,793,179) to act as the anode of the electric arc system.

5 Figure 3 shows illustrative duty cycles of the power supply 105. The time T_1 during which the arc source is energized (on) and the time T_2 during which the arc source is off can be varied independently. For example, time T_1 can be hours when the arc source is run continuously or it can be minutes when pulsed. Time T_2 may be zero or finite. Typical
10 valves for the peak of the pulse varies in the range 30-200 Amps.

Reference should now be made to Figures 3A and 3B where Figure 3A is a block diagram of illustrative control circuitry for use with the arc supply of the present invention and
15 Figure 3B is an illustrative flow diagram of a subroutine of the program which may be employed in the controller of Figure 3A. In Figure 3A the control circuit 120 is generally indicated, and includes a programmable, process controller 122. The controller may be obtained from the Texas Instruments
20 Corporation, Model TCAM 5230, this controller being provided with a program for controlling the cathodic arc process. In accordance with one aspect of the invention, the program is modified by adding thereto program steps which may correspond to those exemplified by the flow diagram of Figure 3B.
25 Conventionally the controller 122 includes output 128 which controls the magnitude of the current supplied by arc supply 105 and output 130 which controls the magnitude of the bias voltage provided by power supply 104. The controller 122 is also

(conventionally adapted to receive a signal from a temperature sensor 132, the controller including internal analog to digital circuitry for digitizing the output signal from the temperature sensor to facilitate processing thereof. The temperature sensor 132 may typically be a conventional, infrared sensor which reads the temperature of substrates 103. This temperature hereafter will be referred to as T_S . The controller also conventionally includes an output 134 which turns the arc supply 105 on and off. A conventional output 135 is also provided which is applied to a striker 115 via a coil 115' to initiate an arc from target 102 where the striker may be of the electro-mechanical, electric, or gas discharge type.

In operation, the program conventionally supplied with the controller 102 enables setting of the magnitude of the arc current from output 128. It also enables setting of the magnitude of the bias voltage provided by power supply 104. In the modification of the program, in accordance with one aspect of the invention, the subroutine of Fig. 3B is entered at 137 and the substrate temperature is read at 134. The substrate temperature T_S is then compared with a lower temperature limit T_L at 136. If, for example, it is desired to maintain the average temperature of the substrates 103 at about 100°C ., the lower temperature limit T_L would be about 90°C . If the substrate temperatures are less than T_L , a current is outputted from output 136 through striker 115 to initiate the arc, this being indicated at 138. This instant of time

corresponds to one of the leading edges of the pulses shown in Figure 3. As stated above, the magnitude of the pulses is conventionally controlled from output 128. Once the pulse is initiated, the subroutine of Figure 3A is exited at 139 such that the main program conventionally provided with the controller 122 is returned to. As long as the deposition procedure continues, the routine of Fig. 3B will be repetitively executed. Once the routine is returned to, the substrate temperature is again read and again a comparison is made with the lower temperature limit T_L at 136. Assuming at this time the substrate temperatures are greater than the lower temperature limit, another comparison is made at 140 to determine whether the substrate temperature is greater than an upper temperature limit T_U . Assuming the desired, average temperature of the substrates is about 100°C ., the temperature limit T_U is typically set to about 110°C . If this temperature limit is exceeded, a signal is applied from output 134 of controller 122 to turn the arc supply 105 off, this being indicated at 142. This instant of time corresponds to the trailing edges of the pulses shown in Figure 3. Once arc supply 105 is turned off, the main program is returned to via exit 139. If the substrate temperature T_S is less than the upper limit temperature T_U , the pulse is maintained in its ON state.

From the foregoing it can be seen, the arc source 110 is pulsed to maintain the temperature of the substrates at a level

(Suitable for the type of coating applied thereto, as will be further discussed in EXAMPLE I below.

Other implementations may be employed to provide pulsing of the arc source. For example, a comparison can be made at 136 to determine if $T_S > T_U$. If so, the arc supply is turned off. Comparisons would then be made at 140 to determine when $T_S < T_L$. When this occurred, the arc would be reinitiated. Moreover, a hardware configuration may be employed where hardware sources for providing a pulse train in other than cathodic deposition applications are known. Further, the nature of the control provided to maintain the substrate temperature may differ in other ways from that illustrated in Figure 3B. For example, a conventional closed-loop control may be utilized where the sensed substrate temperature is continuously compared with the desired substrate temperature to provide a continuous error signal which is employed to control the substrate temperature. Alternatively, an approach similar to that of Figure 3B may be employed where a comparison corresponding to step 136 is made to determine if the temperature T_S is less than T_L . If it is, the arc is struck and the supply 105 is turned on for a predetermined period of time. No upper temperature limit T_U is employed. Rather, the substrate temperature T_S is repetitively compared with the lower temperature T_L . When T_S is again less than T_L , the arc supply is again turned on for the predetermined period of time.

(The arc is initiated within the chamber by striker 115. The striker 115 may be an electro-mechanical device which contacts the surface of the cathode source with an arc-initiating wire or a gas discharge ignition system where a high voltage gas discharge establishes an electric current path between the striker and the cathode surface by an appropriate power supply. The cathodic arc source is water-cooled by a special channel machined on the copper block 111 attached on the back of the cathode or arc source material 102. The action of the electric arc on the surface of the cathode material results in a "cathode spot". The cathode spot moves at random across the surface of the coating source material to form coating plasma. The cathode spot motion can also be controlled with the help of a suitable magnetic field arrangements.

The item(s) to be coated within the chamber are typically referred to as substrates, and are generally illustrated at 103, substrates not being illustrated in detail since they do not as such form a part of this invention. The source of coating material 102 is typically referred to as a cathode or target (where the target may be disposed on the cathode or the target may be the cathode). The target 102 is the origin of coating flux or plasma for the arc deposition process. The source materials 102 such as titanium, zirconium, titanium-zirconium or titanium-aluminum are solid and may be in cylindrical, circular, oblong or rectangular form or any other appropriate form. Alternatively, one can employ separate targets for each source material to do co-deposition of a mixed coating system.

(In operation, the substrates to be coated are chemically cleaned and then loaded on rotary work holder 102. The vacuum chamber 100 is then pumped down to a base pressure with pumping system 101. The substrates or parts are then ion cleaned and heated with metal ion bombardment by turning on the arc sources 110 and biasing the substrates of a high voltage by supply 104. Next, the arc source 110 is pulsed at different duty cycles, and the bias voltage from supply 104 and the arc current source 105 are adjusted depending on the temperature limit of the substrates. A reactive gas with suitable dopants is then introduced to maintain chamber pressure in the range of about 0.1 to 15.0 microns through the gas inlet valve 106 and gas in line valves 107. The substrate bias and arc current may be controlled by an automatic process controller which is driven by a pre-set temperature limit. The resultant hard coating begin to deposit at a set substrate temperature. Typical coating thicknesses in the range of about 0.5 to 15.0 microns are then deposited for decorative applications.

EXAMPLE 1

Typical operating conditions observed for various substrate temperatures and coating combinations are shown in TABLE 1 where the range on x for alloys and carbonitrides varied from $0 < x < 1$, and in particular from 0.1 to 0.9 in 0.1 increments unless otherwise stated such as in Samples 5 and 14 where the 0.1 increments extended from 0.1 to 0.5. In general,

sample 10, for example, constitutes nine samples where x is incremented in 0.1 increments from 0.1 to 0.9. The foregoing applies to all samples where an alloy constitutes the target material or a carbonitride constitutes the coating material where values of x are stated.

Moreover, the dopants were O₂ or C or a mixture thereof where background O₂ was typically present in the C doped samples and where the amount of dopant was in the range of about 2 to 7 atomic percent. Typically, the C source was a carbon containing gas such as CH₄ or C₂H₂. The foregoing applies to all samples which stated the coating material is doped.

The foregoing remarks regarding the relative alloy and carbonitride amounts and dopant amounts also apply to EXAMPLE II below and all other references to "x" and dopants in the specification and claims. Furthermore, an inert gas such as argon may also be present.

TABLE I

SAMPLE NO.	SUBSTRATE MATERIAL	AVERAGE SUBSTRATE TEMPERATURE	COATING MATERIAL	AVERAGE ARC SOURCE PULSING TIME	
				T ₁ (MIN.)	T ₂ (MIN.)
1	Plastics	~50°C.	Ti	0.5	0.25
2	Plastics	~50°C.	TiN	0.25	0.25
3	Plastics	~50°C.	TiN Doped	0.25	0.25
4	Plastics	~50°C.	ZrN	0.5	0.5
5	Plastics	~50°C.	Ti _x Zr _{1-x} N (0 < x ≤ 0.5)	0.5	0.5

TABLE I (Continued)

SAMPLE NO.	SUBSTRATE MATERIAL	AVERAGE SUBSTRATE TEMPERATURE	COATING MATERIAL	AVERAGE ARC SOURCE PULSING TIME	
				T ₁ (MIN.)	T ₂ (MIN.)
6	Zinc or Zinc Alloys: Class rings, eye-glass frames, pen caps, lighters and watch bezels	~100°C.	TiN	0.5	0.5
7	" "	~100°C.	TiN Doped	0.5	0.25
8	" "	~100°C.	ZrN	0.5	0.25
9	" "	~100°C.	Ti _x Zr _{1-x} N	0.5	0.25
10	" "	~100°C.	Ti _x Al _{1-x} N	0.75	0.25
11	Brass: Pen caps, class rings, eye-glass frames	~150°C.	TiN	1.0	0.5
12	" "	~150°C.	ZrN	1.0	0.5
13	" "	~150°C.	Ti _x Zr _{1-x} N	1.0	0.5
14	" "	~150°C.	Ti _x Al _{1-x} N (0 < x ≤ 0.5)	1.0	0.25
15	" "	~150°C.	TiN Doped	1.0	0.5
16	Stainless Steels (300 Series): Class rings, pen caps, eyeglass frames and silver-ware	~400°C.	TiN	On at all Times	
17	" "	~400°C.	ZrN	On at all Times	
18	" "	~400°C.	Ti _x Zr _{1-x} N	On at all Times	
19	" "	~400°C.	Ti _x Al _{1-x} N	On at all Times	
20	Tool Steels (High speed steels and cemented carbides)	≥ 450°C.	TiC	On at all Times	

TABLE I (Continued)

SAMPLE NO.	SUBSTRATE MATERIAL	AVERAGE SUBSTRATE TEMPERATURE	COATING MATERIAL	AVERAGE ARC SOURCE PULSING TIME	
				T ₁ (MIN.)	T ₂ (MI
21	"	≥ 450°C.	TiC _x N _{1-x}	On at all Times	
22	"	≥ 450°C.	Ti _x Zr _{1-x} N	On at all Times	
23	"	≥ 450°C.	Ti _x Al _{1-x} N	On at all Times	

From the results in TABLE I it was found that when the coating thickness was less than five microns, the luster of the base materials was maintained. Thicker layers (such as 25 or 50 microns) may also be deposited. With such layers in the luster (reflectance) of the substrate (base material) cannot be duplicated; however, the surface finish can be duplicated. Typical layers of the above thickness may constitute several layers where the material of the respective layers may be the same or different.

Figure 4 shows the optical reflectance spectra of doped TiN, doped ZrN and Ti_xZr_{1-x}N films produced by the present invention. Also illustrated is the reflectance spectra of a 14k gold film. Thus, as can be seen, the optical reflectance spectra of the films of this invention can be required in U.S. Patent 4,415,521 of Sasanuma. The various color spectra obtained in different coating systems are shown in TABLE II as an EXAMPLE II.

EXAMPLE II

TABLE II

SAMPLE NO.	COATING MATERIAL	COLOR TYPE
1	TiN	Golden Yellow
2	TiN Doped	Gold (10k-24k)
3	ZrN	Yellowish-green
4	ZrN Doped	White Gold
5	$Ti_xZr_{1-x}N$	Gold (10k-24k)
6	TiC	Grey
7	TiC_xN_{1-x}	Brown, Bronze, Dark Brown
8	$Ti_xAl_{1-x}N$	Dark Brown, Black

From the results of TABLE II, it is noted that a wide range of colors for decorative coatings can be produced. The thickness of the coating film in all cases was in the range of 0.10 to 5 microns. With respect to TiN, the gold yellow color is generally rich in green and bronze colors while the ZrN is a yellowish-green with the green predominating. Both TiN and ZrN can be doped with O_2 to eliminate the greenness and with C to increase redness. Accordingly, by combining the O_2 and C dopants, control can be effected from 10k - 24k with doped TiN or doped ZrN. Moreover, with respect to $Ti_xZr_{1-x}N$, the value of k increases as the value of x increases. In a similar manner TiC_xN_{1-x} and $Ti_xAl_{1-x}N$, vary through different colors as the value of x changes.

Referring again to Figure 4, the 14k gold color of the $Ti_xZr_{1-x}N$ coating was effected with values of x in the range

(
of about 0.25 to about 0.30. This color was effected by
the doped ZrN coating with about 1% O₂ and about 4% C doping
where all precents are atomic percentages for all dopants
referred to in the specification and claims. The 14k gold
5 color of the doped TiN was effected with about 4% O₂ doping.
Moreover, the Ti and N were in non-stoichiometric proportions
where the amount of Ti varied from about 1.15 to about 1.25
atomic ratio for each atomic percentage of N. To achieve
non-stoichiometric films a reduced nitrogen pressure in the
10 range 0.1 to 1.0 microns was employed.

With respect to the 10k gold color, it was effected with
a) $Ti_xZr_{1-x}N$ where x varied from about 0.15 to about 0.20,
b) doped ZrN with about 2% O₂ doping, and (c) doped TiN with
15 about 4% O₂ doping and 3% C doping where the amount of Ti
varied from about 1.25 to about 1.40 atomic ratio for each
atomic percentage of N.

With respect to the 18k gold color, doped TiN with about
20 2% O₂ doping and about 5% carbon doping or $Ti_xZr_{1-x}N$ where
x varies from about 0.4 to about 0.45 were effectively employed.

With respect to the 24k gold color, $Ti_xZr_{1-x}N$ where x
varies from about 0.5 to about 0.55 was employed.
25

EXAMPLE III

Next, the wear resistance of these coatings was measured
30 using a pin-on-disc method, in which a pin with a load of 500
gms was loaded on rotating coated samples (coated discs) and
scratches if any in the coating were observed in an optical

(microscope of 50 times magnification after 50 revolutions. No scratches were present in any of the hard coating in TABLE II.

EXAMPLE IV

Figures 5 and 5A show the atomic composition profiles for various coatings for different colors as was measured by an Electron Spectroscopy for Chemical Analysis (ESCA) where Fig. 5 is the ESCA Sputter depth profile for a TiN film doped with O_2 and C and Fig. 5A is the same profile for a TiZrN film. The O_2 in the film results from the background level of O_2 in the system. This background level is also included in the O_2 illustrated in Fig. 5.

It is to be understood that the above detailed description of the various embodiments of the invention is provided by way of example only. Various details of the coating materials, design and construction may be modified without departing from the true spirit and scope of the invention as set forth in the appended claims. Further, although the preferred embodiments of the invention have been described in connection with an arc coating system, it is to be understood, it is also applicable to other systems such as where material is flash evaporated from a target by an arc which must be confined to a predetermined area of the target surface.

WHAT IS CLAIMED IS:

1. A method of coating a substrate comprising the steps of
sequentially applying arc pulsations to a target to evaporate the target material; and
depositing the evaporant on the substrate to provide a coating of at least the target material thereon.
2. A method as in claim 1 where the thickness of the coating is no greater than about 50 microns.
3. A method as in claim 2 where said coating is formed in multiple layers.
4. A method as in claim 3 where each of said layers comprises the same material.
5. A method as in claim 3 where at least one of said layers comprises a material different than that of the other layers.
6. A method as in claim 2 where the thickness of said coating is not greater than about 5 microns.

7. A method as in claim 6 where said thickness is in the range of 0.1 micron to about 5 microns.

8. A method as in claim 1 where the duty cycle of said arc pulsations is such that the temperature of said substrate is substantially less than 350° C.

9. A method as in claim 8 where the temperature of said substrate is about 50° C. to about 150° C.

10. A method as in claim 8 where said substrate comprises a plastic material.

11. A method as in claim 10 where said substrate temperature is about 50° C.

12. A method as in claim 10 where said target comprises titanium.

13. A method as in claim 1 including reacting said evaporant with a gas to form a compound so that said compound is deposited as said coating on said substrate.

14. A method as in claim 13 including doping said compound with a dopant so that the deposited coating includes said dopant.

15. A method as in claim 14 where said dopant is oxygen, carbon, or a mixture thereof.

16. A method as in claim 14 where said dopant constitutes about 2 - 7% atomic weight or the coating.

17. A method as in claim 13 where said target material is selected from the group consisting essentially of titanium, zirconium, and titanium zirconium alloys.

18. A method as in claim 17 where said gas comprises nitrogen so that said coating comprises TiN, ZrN, or $Ti_xZr_{1-x}N$ where $0 < x < 1$.

19. A method as in claim 18 where $0.1 \leq x \leq 0.9$.

20. A method as in claim 18 where said coating comprises TiN and where said method includes doping said TiN with a dopant comprising oxygen or carbon or a mixture thereof.

21. A method as in claim 20 where said dopant constitutes about 2 - 7% atomic weight of said coating.

22. A method as in claim 8 where said substrate comprises zinc or a zinc alloy.

(23. A method as in claim 22 where said substrate temperature is about 100°C .

24. A method as in claim 22 including reacting said evaporant with a gas to form a compound so that said compound is deposited as said coating on said substrate.

25. A method as in claim 24 including doping said compound with a dopant so that the deposited coating includes said dopant.

26. A method as in claim 25 where said dopant is oxygen, carbon, or a mixture thereof.

27. A method as in claim 25 where said dopant constitutes about 2 - 7% atomic weight of the coating.

28. A method as in claim 24 where said target material is selected from the group consisting essentially of titanium, zirconium, titanium-zirconium alloys, and titanium-aluminum alloys.

29. A method as in claim 28 where said gas comprises nitrogen so that said coating comprises TiN , ZrN , $\text{Ti}_x\text{Zr}_{1-x}\text{N}$, or $\text{Ti}_x\text{Al}_{1-x}\text{N}$ where $0 < x < 1$.

30. A method as in claim 29 where $0.1 \leq x \leq 0.9$.
31. A method as in claim 29 where said coating comprises TiN and where said method includes doping said TiN with a dopant comprising oxygen or carbon or a mixture thereof.
32. A method as in claim 31 where said dopant constitutes about 2 - 7% atomic weight of said coating.
33. A method as in claim 8 where said substrate comprises brass.
34. A method as in claim 33 where said substrate temperature is about 150°C .
35. A method as in claim 33 including reacting said evaporant with a gas to form a compound so that said compound is deposited as said coating on said substrate.
36. A method as in claim 35 including doping said compound with a dopant so that the deposited coating includes said dopant.
37. A method as in claim 36 where said dopant is oxygen, carbon, or a mixture thereof.

38. A method as in claim 36 where said dopant constitutes about 2 - 7% atomic weight of the coating.

39. A method as in claim 35 where said target material is selected from the group consisting essentially of titanium, zirconium, titanium-zirconium alloys, and titanium-aluminum alloys.

40. A method as in claim 39 where said gas comprises nitrogen so that said coating comprises TiN, ZrN, or $Ti_xZr_{1-x}N$, or $Ti_xAl_{1-x}N$ where $0 < x < 1$.

41. A method as in claim 40 where $0.1 \leq x \leq 0.9$.

42. A method as in claim 40 where said coating comprises TiN and where said method includes doping said TiN with a dopant comprising oxygen or carbon or a mixture thereof.

43. A method as in claim 42 where said dopant constitutes about 2 - 7% atomic weight of said coating.

44. A method of coating a substrate comprising the steps of
continuously applying an arc to a target to evaporate the target material;

providing a substrate consisting essentially of stainless steel; and

depositing the evaporant on the substrate to provide a coating of at least the target material thereon where said substrate consists essentially of class rings, pen caps, eye glass frames and silverware.

45. A method as in claim 44 where the temperature of said substrate is substantially 400°C .

46. A method as in claim 44 including reacting said evaporant with a gas to form a compound so that said compound is deposited as said coating on said substrate.

47. A method as in claim 46 where said target material is selected from the group consisting essentially of titanium, zirconium, titanium-zirconium alloys, and titanium-aluminum alloys.

48. A method as in claim 47 where said gas comprises nitrogen so that said coating comprises TiN , ZrN , $\text{Ti}_x\text{Zr}_{1-x}\text{N}$ or $\text{Ti}_x\text{Al}_{1-x}\text{N}$ where $0 < x < 1$.

49. A method as in claim 48 where $0.1 \leq x \leq 0.9$.

50. A method of coating a substrate comprising the steps of

continuously applying an arc to a target consisting essentially of titanium, titanium-zirconium alloys, and titanium-aluminum alloys to evaporate the target material; providing a substrate consisting essentially of tool steel;

reacting said evaporant with nitrogen or a carbon containing gas to form a compound; and

depositing the compound on the substrate to provide a coating of at least the target material thereon, said coating selected from the group consisting essentially of TiC , $\text{Ti}_x\text{N}_{1-x}$, $\text{Ti}_x\text{Zr}_{1-x}\text{N}$, and $\text{Ti}_x\text{Al}_{1-x}\text{N}$ where $0 < x < 1$.

51. A method as in claim 50 where $0.1 \leq x \leq 0.9$.

52. A method as in claim 50 where the temperature of said substrate is greater than or equal to about 450°C .

53. Apparatus for coating a substrate comprising means for sequentially applying arc pulsations to a target to evaporate the target material; and

means for depositing the evaporant on the substrate to provide a coating of at least the target material thereon.

54. Apparatus as in claim 53 where the duty cycle of said arc pulsations is such that the temperature of said substrate is substantially less than 350°C.

55. Apparatus as in claim 54 where the temperature of said substrate is about 50°C. to about 150°C.

56. Apparatus as in claim 53 where said substrate comprises a plastic material.

57. Apparatus as in claim 53 where said substrate comprises zinc or a zinc alloy.

58. Apparatus as in claim 53 where said substrate comprises brass.

59. Apparatus for coating a substrate comprising means for continuously applying an arc to a target to evaporate the target material;

means for providing a substrate consisting essentially of stainless steel; and

means for depositing the evaporant on the substrate to provide a coating of at least the target material thereon where said substrate consists essentially of class rings, pen caps, eyeglass frames, watch cases and bands, lighter cases, and silverware.

60. Apparatus for coating a substrate comprising means for continuously applying an arc to a target consisting essentially of titanium, titanium-zirconium alloys, and titanium-aluminum alloys to evaporate the target material; means for providing a substrate consisting essentially of tool steel; means for reacting said evaporant with a gas to form a compound; and depositing the compound on the substrate to provide a coating of at least the target material thereon, said coating selected from the group consisting essentially of TiC , TiC_xN_{1-x} , $Ti_xZr_{1-x}N$, and $Ti_xAl_{1-x}N$ where $0 < x < 1$.

61. A method of coating a substrate comprising the steps of

applying an arc to a target consisting essentially of at least one of titanium, titanium-aluminum, zirconium, or titanium-zirconium to evaporate the target; and

providing a decorative part as said substrate, the material comprising said part selected from the group consisting essentially of plastics, zinc, zinc alloys, brass and stainless steel;

reacting the evaporant with a gas including at least one of nitrogen or a carbon containing gas; and

depositing the reaction product as a coating on said substrate.

62. A method as in claim 61 where said decorative parts consists essentially of class rings, watch cases, watch bands, silverware, spectacle frames, pen caps, and lighters.

63. A method as in claim 61 where said substrate comprises a titanium-zirconium alloy and said gas comprises nitrogen to provide on the substrate a gold colored coating comprising $Ti_xZr_{1-x}N$ where $0 < x < 1$ and the gold color varies from about 10k to 24k such that as x increases k increases.

64. A method as in claim 63 where said gold color is about 10k and x varies between about 0.15 and 0.20.

65. A method as in claim 63 where said gold color is about 14k and x varies between about 0.25 and 0.30.

66. A method as in claim 63 where said gold color is about 18k and x varies between about 0.40 and 0.45.

67. A method as in claim 63 where said gold color is about 24k and x varies between about 0.50 and 0.55.

68. A method as in claim 61 where said substrate is titanium and said gas comprises said carbon containing gas to provide on the substrate a grey colored coating comprising TiC.

69. A method as in claim 61 where said substrate is titanium and said gas comprises a mixture of nitrogen and said carbon containing gas to provide on the substrate a colored coating comprising $\text{TiC}_x\text{N}_{1-x}$ where $0 < x < 1$ and the color of the coating is brown, bronze, dark brown depending on the value of x .

70. A method as in claim 61 where said substrate comprises a titanium-aluminum alloy and said gas comprises nitrogen to provide on the substrate a colored coating comprising $\text{Ti}_x\text{Al}_{1-x}\text{N}$ where $0 < x < 1$ and the color of the coating is dark brown or black depending on the value of x .

71. A method as in claim 61 including doping said coating with O_2 or C or a mixture thereof.

72. A method as in claim 71 where said target consists essentially of titanium and said gas consists essentially of nitrogen so that said coating is doped TiN.

(73. A method as in claim 72 where the color of said doped TiN is gold which varies from about 10k to 24k depending on the relative proportion of C and O₂ dopants.

5 74. A method as in claim 73 where said gold color is about 10k and the amounts of said O₂ dopant is about 4 atomic percent and said C dopant is about 3 atomic percent.

10 75. A method as in claim 74 where the amount of said Ti is about 1.25 to about 1.40 atomic ratio for each atomic percentage of N.

15 76. A method as in claim 73 where said gold color is about 14k and the amount of said O₂ dopant is about 4 atomic percent.

20 77. A method as in claim 76 where the amount of said Ti is about 1.15 to about 1.20 atomic ratio for each atomic percentage of N.

78. A method as in claim 73 where said gold color is about 18k and the amounts of said O₂ dopant is about 2 atomic percent and said C dopant is about 5 atomic percent.

25 79. A method as in claim 71 where said target consists essentially of zirconium and said gas consists essentially of nitrogen so that said coating is doped ZrN.

80. A method as in claim 79 where the color of said doped ZrN is white gold which varies from about 10k to 24k depending on the relative proportion of C and O₂ dopants.

81. A method as in claim 80 where said gold color is about 10k and the amount of said O₂ dopant is about 2 atomic percent.

82. A method as in claim 80 where said gold color is about 14k and the amounts of said O₂ dopant is about 1 atomic percent and said C dopant is about 4 atomic percent.

83. A method as in claim 79 where the color of the doped ZrN is white gold.

84. A method as in claim 83 where the amount of dopant is about 5 atomic percent O₂.

85. Apparatus for coating a substrate comprising means for applying an arc to a target consisting essentially of at least one of titanium, titanium-aluminum, zirconium, or titanium-zirconium to evaporate the target; a decorative part comprising said substrate, the material comprising said part consisting essentially of plastics, zinc or zinc alloys, brass and stainless steel;

means for reacting the evaporant with a gas including at least one of nitrogen or a carbon containing gas; and

means for depositing the reaction products as a coating on said substrate.

86. Apparatus as in claim 85 where said decorative parts consisting essentially of class rings, watch cases, watch bands, silverware, spectacle frames, pen caps, and lighters.

87. Apparatus as in claim 85 including doping said coating with O_2 or C or a mixture thereof.

88. A method of coating a substrate substantially as hereinbefore described.

89. Apparatus for coating a substrate substantially as hereinbefore described with reference to the accompanying drawings.